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(57) Abstract

New polyesters comprising polyoxyfluoroalkylene blocks are prepared by polycondensation of diols with dicarboxylic acids or with derivatives thereof, said fluorinated polyesters being characterized by such improved surface properties that any subsequent treatments of the surface of the articles obtained therefrom are needless.

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Fluorinated Polyesters

BACKGROUND OF THE INVENTION

1. Field of the invention

The present invention relates to fluorinated polyesters of the thermoplastic or thermoelastomeric type.

2. The Prior Art

There are known thermoplastic polyesters, which are widely utilized as films, fibres, supports for magnetic tapes, structural materials in fields such as the electronic or the biomedical. They are generally prepared by polycondensation of aromatic diacids or their derivatives with diols. Typical examples are polyethyleneterephthalate and polybutyleneterephthalate, which are obtained by polycondensation of terephthalic acid or of a derivative thereof, for example a diester, with ethylene glycol or butandiol, respectively.

There are also known thermoelastomeric polyesters obtained by condensation of a diacid or a derivative thereof, such as e.g. a diester, with a low molecular weight glycol and with a polyglycol, generally a polyoxyalkylene glycol having a molecular weight from 1000 to 3000.

The thermoplastic and thermoelastomeric polyesters are characterized by high mechanical and electrical characteristics, a good stability to solvents and to hydrolysis.

For a plurality of uses such as films, supports for magnetic tapes, fibres, in various sectors of goods, they exhibit however considerable drawbacks, as they have a low oil and water-repellency, a low resistance to soiling and low free flowing properties, characterized by a high friction coefficient, so that a subsequent finishing treatment of such articles is absolutely necessary.

In particular, as regards the use for magnetic recording tapes, where the material flows on metal or plastic surfaces, a surface treatment of said surface with a lubricant is required in order to

reduc fricti n and t secur th sliding of th tape and preserv it as much as possible from the wearing. For thes uses, very thin layers on the substrate surface, generally from 50 to 1,000 Å, are sufficient.

For other uses, for example in particular in the biomedical field, the conventional hydrogenated polyesters, although exhibiting-in comparison with other utilizable materials - improved impermeability and mechanical properties, do not exhibit good biocompatibility and antithrombogenicity.

With a view to overcoming these drawbacks, the hydrogenated poly= esters are therefore subjected to finishing processes or surface treatments.

These finishing processes or these surface treatments are gene= rally carried out, for example, with a fluorinated oil or with a solution or a dispersion of a fluorinated plastic polymer, such as, for example, a polytetrafluoroethylene dispersion, depending on the type of application. However, these fluorinated coatings exhibit the drawback of not sufficiently adhering to the substrate, owing to the surface properties which are typical of the fluorinated polymer and which interfere with the adhesion. By consequence, since it is not possible to maintain the fluorinated layer adherent to the article for a sufficiently long period of time, a degradation of the surface properties occurs, such as resistance to chemical agents, oil- and water-repellency, resistance to soi= ling, free flowing which, conversely, are indispensable for a plu= rality of uses.

An alternative method of increasing the duration of the abovesaid surface properties consists in chemically binding a fluorinated monomer to the polymeric substrate by grafting. This process can be carried out, for example, by using radiation or electric dis= charge.

With such method, howev r, the btainment f a uniform layer is strictly related to the substrat natur . In fact, n substrates having an irregular shape no uniform layer of fluorinated coating can be obtained.

According to another method of obtaining fluorinated coatings on non-fluorinated polyesters, a non-fluorinated polyester is coex= truded with a fluorinated copolymer, for example a tetrafluoro= ethylene/hexafluoropropene polymer. This method, however, besides requiring a particularly complex technology, can be rarely used, as it can be applied only for particular types of articles, for example fibres.

By consequence, there was the requirement of having available rea dily processable polyesters which permit to overcome the above= said problems of finishing or of surface treatment, and at the sa me time having the above-cited characteristics of chemical inertia, mechanical properties, oil- and water-repellency, biocompatibility.

THE PRESENT INVENTION

It has now surprisingly b n found that polyesters comprising fluoropolyoxyalkylene units represent a n v l technological so= lution which permits to overcome the above-cited limitations as they permit to avoid all surface treatments or finishing opera= tions.

Thus, the object of the present invention is a polyester charac terized by a block structure and comprising, with respect to the total number of moles constituting the polyester, amounts not hi gher than 45% by moles of at least one fluoropolyoxyalkylene com prising the repeating fluoropolyoxyalkylene units selected from the following classes:

I (C_2F_4O), (CF_2O), said units being randomly distributed along the fluoropolyoxyalkylene chain;

II (C_3F_6O), (C_2F_4O), $(CFXO)$ where $X = -F$ or $-CF_3$, said units being randomly distributed along the perfluoropolyoxyalkylene chain;

III $-CH_2-CF_2-CF_2-O-$

said units being linked to one another inside the fluoropoly= oxyalkylene chain as shown by the following structural formu= la:

$-(O-CF_2-CF_2-CH_2)_p-O-R'_f-O-(CH_2-CF_2-CF_2-O)_q-$ where R'_f is a fluoroalkylene group, preferably containing 1 to 8 carbon atoms, p and q are integers, p+q is at least 2 and, preferably, up to 200;

IV $(\underset{\displaystyle CF_3}{\underset{|}{C}F}CF_2O)$

said units being linked to one another inside the fluoropoly= oxyalkylene chain as shown by the following structural formu= la:

$$-\left(O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{C}F}\right)_a-O-CF_2-(R_f)_x-CF_2-O-\left(\underset{\displaystyle CF_3}{\underset{|}{C}F}-CF_2-O\right)_b-$$

where R_f is a fluoroalkylene group, preferably containing 1 to 8 carbon atoms, x is 0 or 1, a and b are integers and a+b is at least 2 and, preferably, up to 30;

V (CF_2CF_2O);

VI $(CF_2CF_2CF_2O)$.

The fluorinat d poly st rs f the inv ntion are pr pared by directly carrying out a polycondensation of fluoropolyoxyalkyl= enes comprising the abovesaid repeating units with the cited diols or carboxylic diacids or derivatives thereof. Such fluoropolyoxyalkylenes having functional groups at both ends contain hydroxy end groups or carboxylic end groups and have an average molecular weight of from about 400 to 10,000, the minimum value depending on the type of repeating structure, so that polyesters having a molecular weight equal to at least 20,000 are obtained.

The polymers so obtained, besides retaining the excellent pro= perties of the polyesters, particularly mechanical and electri cal properties, chemical inertia to common solvents, exhibit also improved surface characteristics, such as oil- and water- -repellency, low friction coefficient, chemical inertia to ag= gressive agents such as hydrocarbon fluids or chlorinated sol= vents, so avoiding the difficulties connected with the prepa= ration and the carrying out of the fluorinated surface treatment needed for the conventional polyesters. These materials are therefore particularly suitable for a wide variety of uses such as e.g. oil- and water-repellent films and fibres, substrates for magnetic tapes, biocompatible structural materials for bio= medical uses.

For the preparation of the polyesters of the invention the fol= lowing compounds are utilized:

1) a hydrogenated diacid or diester or diacylchloride having the following general formula:

$$Y-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-R_2-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-Y'$$

wherein Y and Y', equal or different one another, are ha= logen or OR', wherein R' is H or an alkyl radical contai= ning from 1 to 8 carbon atoms or an aryl radical having

fr m 6 to 10 carbon atoms;

R_2 is a divalent radical having from 2 to 30 carbon at ms such as, for example:

a) an alkylene radical of the type:

$$-(CH_2)_{m'}-, \quad -(CH_2)_{m'}-\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}-(CH_2)_{m'}-$$

$$-(CH_2)_{m'}-\overset{\substack{CH_3\\ |}}{CH}-\overset{\substack{CH_3\\ |}}{CH}-(CH_2)_{m'}-$$

wherein m' is an integer from 2 to 20;

b) a fluorinated or non-fluorinated arylene radical such as for example para- or meta-phenylene, para- or meta-xylene;

c) a cycloaliphatic or polycyclic, fluorinated or non-fluorinated, divalent radical, such as for example 1,4-cyclohexylene, 1,3-cyclohexylene, 2-methyl-1,4-cyclohexylene, 2-methyl-1,3-cyclohexylene, diarylenmethane, etc.

Particularly suitable for the purposes of the invention are the aromatic dicarboxylic acids, such as for example the terephthalic, phthalic and isophthalic acids and their derivatives;

2) a hydrogenated diol containing an alkylene radical having from 2 to 14 carbon atoms, such as ethylene, propylene, tetramethylene, hexamethylene, dodecamethylene, cyclohexylene, 2,2-dimethyltrimethylene or cyclohexan-dimethylene;

3) a difunctional derivative having an average molecular weight from about 400 to 10,000, preferably from 500 to 5,000, comprising the fluoropolyoxyalkylene units described above in classes I, II, III, IV, V and VI and having end groups of the following type:

$$-(CH_2)_v-(OCH_2CH_2)_z-A$$

wherein v and z are integers or zero, preferably v is 0 or 1, and z is 0 or an integer up to 3;

A is OH, in such case v being at least 1, or COY, Y being the same as defined before.

Difunctional derivatives having end groups as described before and belonging to class I are particularly selected from those comprised in the following general formula:

$$A - (CH_2CH_2O)_z - (CH_2)_v - CF_2O - (C_2F_4O)_m - (CF_2O)_n- -CF_2-(CH_2)_v-(OCH_2CH_2)_z -A$$

wherein v, z and A have the meaning defined hereinbefore and m and n are positive integers such that the molecular weight falls within the indicated range.

One can prepare these fluoropolyoxyalkylene derivatives according to known methods, as described for example in patents US 3,810,874 and US 3,847,978.

Difunctional derivatives having the above described end groups and belonging to class II are particularly selected from those comprised in following general formula:

$$A-CH_2-CF_2-(C_3F_6O)_r(C_2F_4O)_s(CFXO)_t-CF_2-CH_2-A$$

wherein X is -F or $-CF_3$, indexes r, s, t are positive integers such that the molecular weight is as above indicated, and A is as defined hereinbefore.
One can prepare such compounds by photo-oxidation of C_3F_6 and C_2F_4 mixtures, as described in US patent 3,665,041, and by successively converting -COF end groups into groups containing the end group A, such conversion being accomplished according to known methods as described for example in patents US 3,847,978 and US 3,810,874.

Difunctional derivatives having the above described end groups and belonging to class III are particularly selected from the compounds having general formula:

$$A-CF_2CH_2(OCF_2CF_2CH_2)_p-CR'_fO-(CH_2CF_2CF_2O)_qCH_2CF_2-A$$

wherein p, q, A and R'_f are the same as defined hereinabove.

These compounds are described in published European patent application 148,482, and the end groups containing -COF can be converted so as to have end groups A, as is described in patents US 3,847,978 and US 3,810,874.

Difunctional derivatives having the above cited end groups and belonging to class IV are particularly selected from the compounds having general formula:

$$A-\left[\underset{\displaystyle CF_3}{\underset{|}{CF}}-\left(OCF_2\underset{\displaystyle CF_3}{\underset{|}{CF}}\right)_a-OCF_2(R_f)_x-CF_2O-\left(\underset{\displaystyle CF_3}{\underset{|}{CF}}CF_2O\right)_b-\underset{\displaystyle CF_3}{\underset{|}{CF}}\right]_n-A$$

where a, b, A, R_f, x have the meaning defined hereinbefore, n is a positive integer.

Such compounds are described in published European patent application 151,877 and the end groups containing -COF are converted in order to have end groups A as is described in patents US 3,847,978 and US 3,810,874.

Difunctional derivatives having end groups as described be= fore and belonging to classes V and VI, are prepared by the processes described respectively in US patent 4,523,039 and European patent application 148,482, both successively fol= lowed by the treatments described in Italian patent applica tion 22920 A/85;

4) a hydrogenated polyoxyalkylene glycol having an average mo= lecular weight from about 400 to 4,000 and preferably from 1,000 to 2,000, having the following general formula:

$$HO(C_dH_{2d}O)_gH$$

where d = 1-4 and g = 6-70, C_dH_{2d} being linear or having side-chains.

Representative xamples of such class f compounds are: polyethylene glycol, polypropylene glycol, polytetramethyl ene glycol.

The fluorinated polyester of the present invention are prepared by properly mixing the above-specified compounds in such way that at least one of them is a fluoropolyoxyalkylene derivative and the molecular weight of the final polyester is not lower than 20,000.

According to the present invention, the fluorinated polyesters comprising the fluoropolyoxyalkylene derivative in amounts not exceeding 5% by moles, preferably from 0.1 to 5% by moles with respect to the total number of moles constituting the polyester are particularly suitable for substrates for magnetic tapes, oil- and water-repellent films and fibres.

The polyesters of the invention having a content of fluoropoly= oxyalkylene units higher than 5% by moles are particularly utili= zable in the biomedical field due to their high biocompatibility.

By properly varying the components from 1) to 4), it is possible to obtain thermoplastic or thermoelastomeric materials. The thermoelastomeric materials contain a rubber-like phase which may consist either of fluoropolyoxyalkylene or of polyoxyalkylene glycol or of mixtures thereof. Generally, in the presence of high fluoropolyoxyalkylene contents, for example of 30% by moles, the polyester is thermoelastomeric; in case of lower amounts, $\leqslant$ 5% by moles, it is necessary to add polyoxyalkylene glycols.

One can prepare the polyesters of the invention by conventional polycondensation techniques, such as for example, in bulk, in solution, in emulsion, interface polycondensation.

Always according to the known polyester synthesis methods, the polycondensation can be carried out starting from dicarboxylic

acids and diols, r by trans sterification starting fr m di sters and diols, or fr m diacylchlorides and di ls.

Particularly suitable for the purposes of the present invention is the transesterification and bulk-polycondensation process starting from mixtures of diesters and diols.

Such process is accomplished by first heating the mixture of rea= gents diesters and diols, in proper molar ratios, in the presence of a catalyst, to a temperature from about 200 to 240°C; in this step, the distillation of the by-products (alcohols) generated during the transesterification takes place.

The reaction is carried out in an inert atmosphere, under vigorous stirring and for a time sufficient for the complete removal of the by-products.

The operation time depends on the monomer type, the temperature, the catalyst and the excess of diol employed.

This process step leads to a low molecular weight prepolymer which is converted to a polymer having a molecular weight suitable for high temperature (250-300°C) polycondensation under stirring and at a residual pressure lower than 1 torr, in order to remove the excess of low molecular weight diol.

The polycondensation time, which is a function of the operative conditions, generally ranges from 0.5 to 10 hours.

It is possible to use different types of catalysts, such as, for example, salts of divalent and trivalent metals, such as calcium, manganese, iron, magnesium, aluminium, zinc; oxides of germanium, lead and antimony; alkaline metals (sodium, potassium) alkoxides, titanium alkoxides (isopropylate, butylate).

Both process steps, i.e. transesterification and polycondensation,

ar gen rally ffect d in the absence of solvents: the materials are in th m lten stat .

The polycondensation can be also carried out in solution, using diacylchlorides and diols.

The fluorinated polyesters of the present invention, as mentioned above, permit to obtain, by suitably varying the starting compo= sition of the mixture, both plastic-type and elastomeric-type ma= terials, each type being characterized by excellent mechanical properties. Those skilled in the art will have no difficulty in determining the best compositions for the various utilizations.

The mechanical properties of these fluorinated polyesters, however, can be modified, according to the requirements and the desired ap= pliances, by adding various inorganic additives known in the art, such as carbon black, silica gel, alumina and glass fibres. For a few uses, in particular, it is advisable to incorporate stabili= zers to heat and to ultraviolet radiations, well known in the art.

Furthermore, it is possible to obtain polyesters with a different fluorine content by properly varying the initial molar ratio of the fluoropolyoxyalkylene derivative to the other reagents.

The fluorinated polyesters obtained according to the present in= vention have the same fields of use as the analogous non-fluorina= ted polyesters with the advantage that the articles prepared from said fluorinated polyesters, for example, by injection molding or compression molding processes, exhibit, as compared with the known products, improved properties as regards oil- and water-repellency, self-lubrication, free flowing and biocompatibility.

This properties improvement occurs also for very low amounts, even of 0.5% by moles, of fluoropolyoxyalkylene compound with respect to the final polyester.

A further advantag of the polyesters of the present invention is the possibility of mixing a thermoplastic or thermoelastomeric po= lyester having a high fluorine content, according to the invention, with other fluorinated or non-fluorinated polymeric materials, and of treating the resulting mixture according to a suitable conver= sion technology. In this way it is possible to have available a wide range of materials endowed with improved properties in compa= rison with those obtained from the individual components of the mixtures.

The polyesters of the invention were characterized by determining:

Melting point: thermal differential analysis at a heating rate of 20°C/minute.

Technological properties:

modulus
tensile strength ASTM D 638 and D 412
elongation at break
Shore hardness ASTM D 2240
contact angle: determination by means of a 40 X grazing light microscope
friction coefficient ASTM D 1894-73
water absorption ASTM D 570 - 24 hours.

The test-pieces were prepared by compression molding, operating at temperatures higher by 30-40°C than the polymer melting point, the polymer having been previously dried at 100°C under vacuum.

The following examples are given for merely illustrative purpo= ses and are not to be considered as limitative of the invention.

EXAMPLE 1

120.6 g (0.62 mols) of dimethyl terephthalate (DMT), 89.4 g (0.99 mols) of 1,4-butandiol and 1.2 10^{-3} mols of titanium tetraisopropylate (in an isopropanol solution) were charged into a tree-neck flask having a 0.5-liter volume, equipped with a stirrer, a dropping funnel and a column for the distillation

of the reaction by-products.

Into the dropping funnel there were introduced 62 g (0.031 mols) of α,ω-bis-hydroxy-polyoxyperfluoroalkylene having an average molecular weight equal to 2000 (formula described at point 3), belonging to class I with A = OH; v = 1; z = 1).

The flask was repeatedly subjected to vacuum and nitrogen-filling cycles and was subsequently dipped into an oil bath previously heated to 200°C.

The reaction was conducted under stirring and in a nitrogen atmosphere, and the methanol distillation begun directly after melting of the mass.

After 30 minutes, when the distillation of the theoretical amount of methanol was concluded, the polyoxyperfluoroalkylene diol was added and the whole was allowed to react for 1 hour at 210°C.

The bath temperature was then brought to 250°C while the pressure was gradually lowered to 0.1 torr.

Polycondensation was carried out for 2 hours, where-after it was cooled to room temperature while simultaneously introducing nitrogen into the reaction flask until the atmospheric pressure was reached.

The fluorinated polyester, having the appearance of a light mass, exhibited the following characteristics:
melting point: 220°C
Fluorine content: 18% by weight
Shore hardness D: 72
tensile strength: 540 kg/cm^2
elongation at break: 310%.

The il- and wat r-rep 11 ncy properties and the friction coeffi= cient of the fluorinated polyester were compared with those of a polybutyleneterephthalate sample (check A).

	Fluorinated polyester	Check A
contact angle with H_2O	104	55
contact angle with ligroin	20	complete wetting
contact angle with nitromethane	55	36
dynamic friction coefficient (μ)		
on steel	0.15	0.33
H_2O absorption (% by weight)	0.08	0.65

EXAMPLE 2

Using the apparatus and the modalities described in example 1, a fluorinated thermoelastomeric polyester was prepared, which con= sisted of a rigid crystalline phase, a rubber-like amorphous hy= drogenated phase, an amorphous fluorinated phase having a very low Tg.

The reacting mass consisted of DMT (48.5 g, equal to 0.25 mols), 1,4-butandiol (36 g, equal to 0.4 mols), polyoxytetramethylene glycol having an average molecular weight equal to 1000 (100 g equal to 0.1 mols) and Irganox 1098® (1 g) as antioxidant. In the second step there was added α, ω-bis-hydroxy-polyoxyper= fluoroalkylene having an average molecular weight equal to 2000 and having the formula described at point 3), belonging to class I with A = OH; v = 1; Z = 1 (12.5 g corresponding to 0.00625 moles). The catalyst is titanium tetraisopropylate (0.1% by

moles referred to DMT).

After a 2-hours polycondensation, a high molecular weight fluorina= ted copolyester was obtained, which exhibited the following proper= ties:

melting point: 194°C

Fluorine content: 4.6% by weight

Shore hardness D: 52

tensile yield strength (25% modulus): 132 kg/cm^2

tensile strength: 490 kg/cm^2

elongation at break: 480%.

Analogously with the preceding example, the fluorinated polymer properties were compared with those of a thermoelastomeric copoly= ether-ester not containing fluorine (check B).

	Fluorinated thermoelastomeric polyester	Check B
contact angle with H_2O	110	62
contact angle with ligroin	15	complete wetting
contact angle with nitromethane	59	39
dynamic friction coefficient (μ) on steel	0.20	0.45

EXAMPLE 3

776 g (4 mols) of dimethylterephthalate, 744 g (12 mols) of ethylene glycol, 0.7 g of manganese acetate (II) and 0.7 g of antimony oxide (III) were charged into a glass reactor ha= ving a 3 l volume, equipped with a stirrer, a dropping funnel and a column for the distillation of the reaction by-products.

Into the dropping funnel there were introduced 80 g (0.04 mols) of α, ω-bis-(methylcarboxylate)-polyoxyperfluoroalkylene ha= ving an average molecular weight equal to 2000 (formula descri bed at point 3) belonging to class I, with A = $COOCH_3$, v = z = = 0).

The reactor was repeatedly subjected to vacuum cycles and was subsequently dipped into an oil bath heated to 180°C.

The mixture was stirred for 2 hours, during which the distilla= tion of methanol took place; after this period of time, the fluorinated diester was added and the whole was allowed to further react for 1 hour.

The bath temperature was then brought to 280°C, while simultane= ously and progressively reducing the pressure to 0.1 mm Hg.

After a 2-hour polycondensation, during which the distillation of the ethylene glycol in excess occurred, it was cooled to room temperature.

The fluorinated polyester (m.p. = 250°C, Fluorine content = 5% by weight), after grinding in a rotary ball mill, was extruded at 290°C by means of a laboratory flat-head extruder, was cooled to 25°C, longitudinally stretched at 95°C to 300%, transversally stretched at 120°C to 300% and subsequently treated at 215°C for a few seconds to give a biaxially oriented film having a thick=

n ss of 100 μm.

The fluorinated polyester film exhibited improved surface proper= ties with respect to a conventional polyethyleneterephthalate film.

In fact, the values of the contact angle with H_2O and of the dy= namic friction coefficient on steel were equal to 103° and to 0.25, respectively, in comparison with 70° and 0.55 of a poly= ethyleneterephthalate film not containing fluorine.

CLAIMS:

1. A polyester having a block structure and c mprising , with r = spect to the total number of moles constituting the polyester, not more than 45 mole % of at least one fluoropolyoxyalkylene comprising the repeating fluoropolyoxyalkylene units selected from the following classes:

I (C_2F_4O), (CF_2O), said units being randomly distributed along the fluoropolyoxyalkylene chain;

II (C_3F_6O), (C_2F_4O), (CFXO) with X = -F or $-CF_3$, said units being randomly distributed along the fluoropolyoxyalkylene chain;

III $-CH_2-CF_2-CF_2-O-$
said units being linked to one another inside the fluoropo=lyoxyalkylene chain as shown by the following structural formula:
$$-(O-CF_2-CF_2-CH_2)_p-O-R'_f-O-(CH_2CF_2CF_2-O)_q-$$
where R'_f is a fluoroalkylene group, p and q are integers, p+q is at least 2;

IV $(\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2O)$
said units being linked to one another inside the fluoro=polyoxyalkylene chain as shown by the following structural formula:
$$-\left(O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{C}F}\right)_a-O-CF_2-(R_f)_x-CF_2-O-\left(\underset{\displaystyle CF_3}{\underset{|}{C}F}-CF_2-O\right)_b-$$
where R_f is a fluoroalkylene group, x is 0 or 1, a and b are integers and a+b is at least 2;

V (CF_2CF_2O) ;

VI $(CF_2CF_2CF_2O)$.

2. The polyester according to claim 1 prepared by using the following compounds:

1) a hydrogenated diacid or diester or diacylchloride having the following general formula:

$$Y - \underset{\underset{O}{\|}}{C} - R_2 - \underset{\underset{O}{\|}}{C} - Y'$$

wherein Y and Y', equal or different one another, are halogen or OR', wherein R' is H, or an alkyl radical containing from 1 to 8 carbon atoms, or an aryl radical having from 6 to 10 carbon atoms;

R_2 is a divalent radical having from 2 to 30 carbon atoms, selected from:

a) an alkylene radical;

b) a fluorinated or non-fluorinated arylene radical;

c) a cycloaliphatic or polycyclic, fluorinated or non-fluorinated divalent radical;

2) a hydrogenated diol containing an alkylene radical having from 2 to 14 carbon atoms;

3) a difunctional derivative having an average molecular weight from about 400 to 10,000, comprising the fluoropolyoxyalkylene units of classes I, II, III, IV, V and VI of claim 1), and having end groups of the following type:

$- (CH_2)_v-(OCH_2CH_2)_z-A$

wherein v and z are integers or zero, A is OH, in such case v being at least 1, or COY, Y being as defined hereinbefore at point 1);

4) a hydrogenated polyoxyalkylene glycol having an average molecular weight from about 400 to 4,000, having the following general formula:

$$HO(C_dH_{2d}O)_gH$$

where d = 1-4 and g = 6-70, C_dH_{2d} being linear or having side chains.

3. The polyester according t claim 2, wh r in the alkylen ra=dical f point a) is selected from:

$$-(CH_2)_{m'}- \ , \quad -(CH_2)_{m'}-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-(CH_2)_{m'}- \ ,$$

and $$-(CH_2)_{m'}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-(CH_2)_{m'}- \ ,$$

wherein m' is an integer from 2 to 20.

4. The polyester according to claim 2, wherein the arylene ra=dical of point b) is selected from para-phenylene, meta-phe=nylene, para-xylene and meta-xylene.

5. The polyester according to claim 2, wherein the divalent ra=dical of point c) is selected from 1,4-cyclohexylene, 1,3--cyclohexylene, 2-methyl-1,4-cyclohexylene, 2-methyl-1,3--cyclohexylene and diarylenmethane.

6. The polyester according to claim 2, wherein the compound 3) has an average molecular weight from 500 to 5,000.

7. The polyester according to claim 2, wherein the compound 4) has an average molecular weight from 1,000 to 2,000.

8. The polyester according to claim 2, wherein v is zero or 1 and z is zero or an integer from 1 to 3.

9. The polyester according to claim 2, wherein the compound 1) is an aromatic dicarboxylic acid.

10. The polyester according to claim 2, wherein the compound 3) has the following general formula:

$$A-(CH_2CH_2O)_z-(CH_2)_v-CF_2O-(C_2F_4O)_m-(CF_2O)_n-$$
$$-CF_2-(CH_2)_v-(OCH_2CH_2)_z-A$$

wh rein v, z and A have the same meaning as defined in claim 2 and m and n are positive integers such that the molecular weight falls within the range indicated in claim 2 at point 3).

11. The polyester according to claim 2, wherein the compound 3) has the following general formula:

$$A\text{-}CH_2\text{-}CF_2\text{-}(C_3F_6O)_r(C_2F_4O)_s(CFXO)_t\text{-}CF_2CH_2\text{-}A$$

where X is -F or -CF_3, the indexes r, s, t are positive inte= gers such that the molecular weight is that indicated in claim 2, point 3), and A is the same as defined in claim 2.

12. The polyester according to claim 2, wherein the compound 3) has the following general formula:

$$A\text{-}CF_2CH_2(OCF_2CF_2CH_2)_p\text{-}OR'_fO\text{-}(CH_2CF_2CF_2O)_qCH_2\text{-}CF_2\text{-}A$$

where p, q and R'_f are as defined under class III) of claim 1 and A is the same as defined in claim 2.

13. The polyester according to claim 2, wherein the compound 3) has the following general formula:

$$A\left[\underset{\displaystyle CF_3}{\underset{|}{CF}}\text{-}\left(OCF_2\underset{\displaystyle CF_3}{\underset{|}{CF}}\right)_a\text{-}OCF_2(R_f)_x\text{-}CF_2O\text{-}\left(\underset{\displaystyle CF_3}{\underset{|}{CF}}CF_2O\right)_b\text{-}\underset{\displaystyle CF_3}{\underset{|}{CF}}\right]_n A$$

where a, b, R_f, x are as defined under class IV) of claim 1, n is a positive integer and A is the same as defined in claim 2.

14. The polyester according to claim 1, wherein the amount of the fluoropolyoxyalkylene compound ranges from 0.1 to 5% by mols with respect to the final polyester.

15. Use of the polyester of claim 1 in the biomedical field.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 86/00712

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: C 08 G 63 /68 A 61 L 33/00, A 61 L 27/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 08 G; A 61 L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 3847978 (DARIO SIANESI et al.) 12 November 1974 see claims 1-25; column 8, lines 57-70 cited in the application	1-14
A	Patents Abstracts of Japan, volume 9, no. 153 (C-288)(1876), 27 June 1985, see the whole abstract & JP, A, 6031535 (KURARAY K.K.) 18 February 1985	1

* Special categories of cited documents: [10]
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10th March 1987	15 APR 1987
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. VAN MOL

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/EP 86/00712 (SA 15440)

This Annex lists the patent family members r lating to the patent documents cit d in the above-mentioned international search report. The members ar as contained in the European Patent Office EDP file on 23/03/87

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3847978	12/11/74	None	

For more details about this annex :
see Official Journal of the European Pat nt Office, No. 12/82